

CHROME PLATED PARTS AND  
CHROME PLATING METHOD

BACKGROUND OF THE INVENTION

5 The present invention relates to chrome plated parts comprising substrates having industrial chrome plating applied on the surfaces thereof. The present invention also relates to a chrome plating method and a production method for obtaining such parts.

10 Chrome plating, especially hard chrome plating, provides a hard metallic coating (i.e., a chrome layer) having a low coefficient of friction. Therefore, chrome plating has been widely used as industrial chrome plating for parts which are required to have high wear resistance.

15 With respect to general-purpose hard chrome plating, a chrome layer formed on a metallic substrate contains many cracks reaching the substrate, called channel cracks. Such a chrome layer enables a corrosive material to migrate into the metallic substrate and cause corrosion. This leads to formation of red rust when the substrate is made of steel.

20 In producing chrome plated parts, generally, a plated substrate is subjected to polishing, such as buffing, so as to provide a smooth surface. It is known that during polishing, cracks in a chrome layer become clogged due to the occurrence of plastic flow over the surface of the  
25 chrome layer. Therefore, in producing general-purpose chrome plated parts, after polishing, no special measures have been taken to prevent rusting.

However, when a chrome layer is subject to thermal

hysteresis, contraction of the chrome layer occurs. In this case, cracks which have been clogged due to plastic flow in the chrome layer are caused to open. Consequently, parts which are used at temperatures higher than room temperature (for example, at 120°C for 100 hours or more) are likely to suffer a lowering in corrosion resistance.

As a countermeasure, it has been attempted to conduct nickel plating or copper plating as a pretreatment, to thereby form a lower layer having a thickness almost equal to that of a chrome layer to be formed, and conducting hard chrome plating on the lower layer. However, in this countermeasure, a plating process must be conducted in two steps, leading to low productivity and high process costs.

As another countermeasure, it has been proposed to conduct chrome plating by using two different plating baths, to thereby deposit two chrome layers having different crystal orientations, thus preventing the formation of cracks reaching the substrate [reference is made to, for example, Unexamined Japanese Patent Application Public Disclosure (Kokai) No. 4-350193]. However, this countermeasure also requires a two-step plating process.

Further, there is a method of conducting electroplating with a pulse current, so-called pulse plating, so as to obtain a crack-free chrome layer [reference is made to, for example, Unexamined Japanese Patent Application Public Disclosure (Kokai) No. 3-207884]. However, the chrome layer formed simply by pulse plating is subject to tensile residual stress. This leads to the formation of large

cracks in the chrome layer due to the application of heat.

Further, there is a method of conducting pulse plating in a Sargent bath by application of an irregular pulse current, to thereby obtain a crack-free decorative chrome layer [reference is made to, for example, Examined Japanese Patent Application Publication (Kokoku) No. 43-20082]. The chrome layer obtained by this method has low (or no) stress. However, the obtained chrome layer has a stress gradient (as the thickness of the chrome layer becomes large, the value of stress shifts from a side of compressive stress toward a side of tensile stress). Therefore, average compressive stress in the chrome layer is undesirably low. Consequently, when the above-mentioned chrome layer is used as a lower layer and a cracked chrome layer is formed as an upper layer by plating on the lower chrome layer, the lower chrome layer is subject to tensile stress from the upper chrome layer, so that propagation of cracks through the upper chrome layer to the lower chrome layer occurs. Further, in the chrome plating bath in Kokoku No. 43-20082, average compressive residual stress can be increased only to a level as low as 100 MPa, even by controlling the waveform of an applied pulse current, a bath temperature and a current density.

In view of the above, the present invention has been made. It is an object of the present invention to provide chrome plated parts which maintain excellent corrosion resistance even when the chrome plated parts are subject to thermal hysteresis. It is another object of the present invention to provide a chrome plating method and a

production method for efficiently obtaining such chrome plated parts.

#### SUMMARY OF THE INVENTION

According to the present invention, there is provided  
5 a chrome plated part comprising a substrate having a crack-free chrome layer applied on a surface thereof. The crack-free chrome layer has compressive residual stress and is formed by plating.

In the chrome plated part of the present invention in  
10 which a crack-free chrome layer having compressive residual stress is formed on a surface of the substrate, due to the compressive residual stress in the chrome layer, no formation of cracks in the chrome layer occurs. Therefore, the chrome layer maintains a crack-free structure. Consequently,  
15 the chrome plated part maintains excellent corrosion resistance even when it is subject to thermal hysteresis.

When compressive residual stress in the chrome layer is too low, the compressive residual stress changes to tensile residual stress due to the occurrence of thermal  
20 hysteresis. This leads to the formation of cracks in the chrome layer. Therefore, it is preferable for the compressive residual stress in the crack-free chrome layer to be 100 MPa or more.

Generally, when a chrome layer is subject to thermal  
25 hysteresis, the formation of cracks is likely to occur due to contraction of the chrome layer. This contraction is affected by the amount of lattice defects present in crystal grain boundaries in the chrome layer. Therefore,

contraction of the chrome layer due to thermal hysteresis can be suppressed by suppressing the amount of lattice defects, that is, by increasing a crystal grain size and decreasing the length of a crystal grain boundary (the  
5 length of a crystal grain boundary is in inverse proportion to a crystal grain size). Therefore, in the chrome plated part of the present invention, it is preferred that the crystal grain size of the crack-free chrome layer be 9 nm or more.

10 The crystal grain size of a chrome layer formed by general-purpose hard chrome plating is as small as about 6 nm. The above-mentioned crystal grain size of the chrome layer in the present invention is much larger than this size. Therefore, the chrome layer in the present invention  
15 contains no cracks even prior to polishing, and maintains a crack-free structure even when it is subject to thermal hysteresis. Therefore, the chrome plated part has desired corrosion resistance. When the crystal grain size is too large, a crystal structure of the chrome layer changes.  
20 Therefore, it is preferable for the crystal grain size of the crack-free chrome layer to be less than 16 nm.

In the chrome plated part of the present invention, the crack-free chrome layer may be a lower chrome layer and the chrome plated part may further comprise a cracked upper  
25 chrome layer which is formed or applied on the lower chrome layer by plating. In this case, the hardness of the upper chrome layer can be increased to a maximum level. This improves wear resistance of the chrome plated part. Further,

cracks in the upper chrome layer serve as oil sumps for holding lubricating oil, leading to suppression of sliding resistance.

5 The chrome plated part may further comprise at least one intermediate chrome layer which is formed between the lower chrome layer and the upper chrome layer by plating. When an intermediate chrome layer is provided, direct propagation of cracks through the upper chrome layer to the lower chrome layer can be suppressed. Therefore, corrosion resistance of the chrome plated part can be stably maintained.

10 The chrome plated part may further comprise an oxide film containing  $\text{Cr}_2\text{O}_3$  as an outermost layer thereof. In this case, the chrome layer itself has high corrosion resistance, so that formation of white rust can be prevented.

15 The present invention also provides a chrome plating method comprising the step of conducting electroplating of a work in a chrome plating bath by application of a pulse current, the chrome plating bath containing organic sulfonic acid, to thereby deposit a crack-free chrome layer on a surface of the work. The crack-free chrome layer has compressive residual stress.

20 In the chrome plating method of the present invention, by adjusting a pulse waveform of an applied current which alternates between a maximum current density and a minimum current density, the compressive residual stress and crystal grain size of a chrome layer can be easily controlled. Therefore, it is possible to obtain a chrome layer having a

compressive residual stress of 100 MPa or more and a crystal grain size of from 9 nm to less than 16 nm.

In the chrome plating method of the present invention, the above-mentioned chrome layer may be formed as a lower chrome layer and the above-mentioned upper chrome layer or the above-mentioned intermediate and upper chrome layers may be formed on the lower chrome layer. In this case, after the chrome layer is deposited as a lower chrome layer by using the pulse plating, electroplating of the work is conducted in the same chrome plating bath as the chrome plating bath for the pulse plating, by one of adjustment of a waveform of the pulse current and application of a direct current, to thereby deposit the upper chrome layer or intermediate chrome layer efficiently.

The chrome layers may be deposited by continuous operation by continuously moving the work in the chrome plating bath or may be deposited by batchwise operation by immersing the work in the chrome plating bath.

Further, the present invention provides a method for producing a chrome plated part, comprising the steps of: conducting the above-mentioned chrome plating method for the two or more than three layers; polishing the upper surface of the work; and conducting heat oxidation, to thereby form an oxide film containing  $\text{Cr}_2\text{O}_3$  on a surface of the chrome layer.

When the upper chrome layer containing cracks is formed by the chrome plating method of the present invention, the cracks in the upper chrome layer become clogged during

polishing due to the above-mentioned plastic flow in the chrome layer. Although the cracks are caused to open again due to heat oxidation after polishing, the chrome plated part has sufficient corrosion resistance for preventing formation of red rust, because the crack-free lower chrome layer is present on the substrate. In addition, since an oxide film containing  $\text{Cr}_2\text{O}_3$  is present as the outermost layer of the chrome plated part, corrosion of the chrome layer itself can be suppressed, thus preventing formation of white rust.

In the method of the present invention for producing a chrome plated part, the method of heat oxidation is not particularly limited. For example, heat oxidation can be conducted under the same conditions as conditions of a general-purpose baking process or by high-frequency heating. With respect to the general-purpose baking process, Federal Specification QQ-C-320a (1967. 7. 25) requires that when steel having a hardness of HRC 40 or more is used as a substrate, the baking process be conducted at  $191 \pm 14^\circ\text{C}$  for 3 hours or more. By conducting heat oxidation under the above-mentioned conditions, an oxide film containing  $\text{Cr}_2\text{O}_3$  is formed on a surface of a substrate. As a method of heat oxidation by high-frequency heating, for example, a substrate is held at a temperature as high as about  $400^\circ\text{C}$  for a short period of time of from several seconds to several tens of seconds.

The foregoing and other objects, features and advantages of the present invention will be apparent from



the following detailed description and appended claims taken in connection with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic illustration of cross section  
5 showing a surface structure of a chrome plated part according to a first embodiment of the present invention.

Fig. 2 is a graph showing an example of a waveform of a pulse current in a chrome plating process for obtaining the chrome plated part of Fig. 1.

Fig. 3 is a top view schematically showing a structure  
10 of a plating apparatus used in the method of the present invention.

Fig. 4 is a schematic illustration showing a surface  
15 structure of a chrome plated part according to a second embodiment of the present invention.

Fig. 5 is a graph showing an example of a waveform of a pulse current in a chrome plating process for obtaining the chrome plated part of Fig. 4.

Fig. 6 is a schematic illustration showing a surface  
20 structure of a chrome plated part according to a third embodiment of the present invention.

Fig. 7 is a top view schematically showing a structure of a system including polishing and heating apparatuses for obtaining the chrome plated part of Fig. 6.

Fig. 8 is a microphotograph showing white rust formed  
25 in Examples.

Fig. 9 is a graph showing a relationship between a thickness of plating and residual stress in the chrome

plated part of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Hereinbelow, embodiments of the present invention are explained, with reference to the drawings.

5           Fig. 1 shows a chrome plated part according to a first embodiment of the present invention. The chrome plated part comprises: a steel substrate M; a crack-free lower chrome layer  $S_1$  formed by plating on a surface of the substrate M; and a multicroaked upper chrome layer  $S_2$  formed by plating  
10 on the lower chrome layer  $S_1$ . The cracks in the chrome layer  $S_2$  are designated by a reference character F. The lower chrome layer  $S_1$  has a compressive residual stress of 100 MPa or more and has a crystal grain size of from 9 nm to less than 16 nm. The upper chrome layer  $S_2$  has a  
15 compressive residual stress less than 100 MPa or a tensile residual stress and has a crystal grain size less than 9 nm.

In the above-mentioned chrome plated part, the crack-free lower chrome layer  $S_1$  is present below the upper chrome layer  $S_2$ . Therefore, although the cracks F are present in  
20 the upper chrome layer  $S_2$ , a corrosive material does not migrate into the substrate M, so that a desired corrosion resistance of the chrome plated part can be ensured. Further, the lower chrome layer  $S_1$  has a predetermined compressive residual stress and a predetermined crystal  
25 grain size, so that the lower chrome layer  $S_1$  maintains a crack-free structure even when it is subject to thermal hysteresis, to thereby ensure excellent corrosion resistance of the chrome plated part. In addition, since the upper

chrome layer  $S_2$  may contain cracks such as the cracks F, the hardness of the upper chrome layer  $S_2$  can be increased to a sufficiently high level (900 HV or more), to thereby impart the chrome plated part with sufficient wear resistance.

- 5 Further, the cracks F present in the upper chrome layer  $S_2$  serve as oil sumps for holding lubricating oil, which enhances sliding properties of the chrome plated part.

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10 The chrome layers  $S_1$  and  $S_2$  are formed by a two-step plating process in a chrome plating bath containing organic sulfonic acid. The two-step plating process comprises plating utilizing a pulse current (hereinafter, frequently referred to as "pulse plating") and plating utilizing a direct current (hereinafter, frequently referred to as "general-purpose plating"). An example of a current density  
15 pattern of an applied current for this process is shown in Fig. 2.

As the chrome plating bath containing organic sulfonic acid, it is preferred to use a chrome plating bath described in Examined Japanese Patent Application Publication (Kokoku)  
20 No. 63-32874, which has compositions as shown in Table 1.

Table 1

Component	Amount (g/L)	
	Suitable	Preferable
Chromic acid	100 - 450	200 - 300
Sulfuric acid	1 - 5	1.5 - 3.5
Organic sulfonic acid	1 - 18	1.5 - 12
Boric acid	0 - 40	4 - 30

Referring to Fig. 2, a zone A indicates a region for the pulse plating for forming the lower chrome layer  $S_1$  and a zone B indicates a region for the general-purpose plating for forming the upper chrome layer  $S_2$ . In the zone A, the applied current alternates between two current densities, namely, a maximum current density  $I_u$  and a minimum current density  $I_L$ . The maximum current density  $I_u$  is held for a predetermined time period  $T_1$  and the minimum current density  $I_L$  is held for a predetermined time period  $T_2$ . In the example of Fig. 2, the minimum current density  $I_L$  is set to zero (off). However, needless to say, the minimum current density  $I_L$  may be arbitrarily set to a value between the maximum current density  $I_u$  and zero. Further, the values of the time periods  $T_1$  and  $T_2$  may be set as being the same or different. In the first embodiment, for pulse plating, the maximum current density  $I_u$ , the minimum current density  $I_L$  ( $I_L = 0$  in this example), the time period  $T_1$  at the maximum current density  $I_u$  and the time period  $T_2$  at the minimum current density  $I_L$  are set to appropriate values, to thereby obtain the lower chrome layer  $S_1$  (Fig. 1) having a predetermined compressive residual stress and a predetermined crystal grain size.

Fig. 3 shows an example of an apparatus for obtaining a chrome plated part having the above-mentioned two chrome layers  $S_1$  and  $S_2$ . In Fig. 3, works (such as piston rods) W are suspended from endlessly movable hangers 1. A mounting station 2, an alkali electrolytic degreasing tank 3, a plating tank 4, a cleaning tank 5 and a removing station 6

are arranged in this order below a line of movement of the hangers 1. The plating tank 4 comprises an etching process tank 4A disposed adjacent to the alkali electrolytic degreasing tank 3 and a plating process tank 4B adjacent to the etching process tank 4A. The plating process tank 4B contains the above-mentioned chrome plating bath containing organic sulfonic acid.

Separate bus bars 7, 8 and 9 are arranged along the alkali electrolytic degreasing tank 3, the etching process tank 4A and the plating process tank 4B, respectively. The bus bar 9 extending along the plating process tank 4B comprises a front bus bar 9A on a side of the etching process tank 4A and a rear bus bar 9B on a side of the cleaning tank 5. The bus bar 7 corresponding to the alkali electrolytic degreasing tank 3, the bus bar 8 corresponding to the etching process tank 4A and the rear bus bar 9B corresponding to the plating process tank 4B are connected to direct current sources 10, 11 and 13, respectively. The front bus bar 9A corresponding to the plating process tank 4B is connected to a pulse current source 12.

The hangers 1 have feeding brushes 14. The feeding brushes 14 are brought into sliding contact with the bus bars 7, 8, 9A and 9B, so that a current is equally applied from the current sources 10, 11, 12 and 13 to each of the hangers 1. In each of the alkali electrolytic degreasing tank 3 and the etching process tank 4A, a plurality of cathodes connected in parallel are provided. The cathodes in the alkali electrolytic degreasing tank 3 and the

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cathodes in the etching process tank 4A are designated by reference numerals 15 and 16, respectively. The plating process tank 4B contains a plurality of anodes 17 corresponding to the front bus bar 9A, which are connected in parallel, and a plurality of anodes 18 corresponding to the rear bus bar 9B, which are also connected in parallel. The current sources 10 and 11 apply currents to the corresponding cathodes 15 and 16, and the current sources 12 and 13 apply currents to the corresponding anodes 17 and 18. In the plating process tank 4B, ammeters 19a and 19b are provided between the anode 17 and the current source 12 and between the anode 18 and the current source 13, respectively.

In order to conduct a chrome plating process using the above-mentioned apparatus, the works W are mounted on the hangers 1 in the mounting station 2. The works W are moved successively to the alkali electrolytic degreasing tank 3 and the etching process tank 4A while being suspended from the hangers 1. In the alkali electrolytic degreasing tank 3, a degreasing process is conducted while making the works W anode. In the etching process tank 4A, an etching process is conducted while making the works W anode. Subsequently, the works W are moved to the plating process tank 4B, where a chrome plating process is conducted while making the works W cathode.

In the chrome plating process, a current having a pulse waveform, such as that indicated in the zone A of Fig. 2, is applied from the current source 12 to the works W through the front bus bar 9A and the anodes 17, to thereby

conduct pulse plating. Pulse plating is continued while the feeding brushes 14 of the hangers 1 (from which the works W are suspended) are in contact with the front bus bar 9A. Consequently, the crack-free lower chrome layer  $S_1$  (Fig. 1) is formed on a surface of each work W. Subsequently, the feeding brushes 14 of the hangers 1 (from which the works W are suspended) move onto the rear bus bar 9B, and general-purpose plating is conducted by application of a direct current from the current source 13 to the works W through the rear bus bar 9B and the anodes 18. General-purpose plating is continued while the feeding brushes 14 of the hangers 1 (from which the works W are suspended) are in contact with the rear bus bar 9B. Consequently, the multicracked chrome layer  $S_2$  having the cracks F is formed on the lower chrome layer  $S_1$  in a superimposed manner as shown in Fig. 1. Thereafter, the works W are cleaned with water in the cleaning tank 5 and moved to the removing station 6, where the works W are removed from the hangers 1.

In the above-mentioned chrome plating process, the two chrome layers  $S_1$  and  $S_2$  can be formed by continuously moving the works W in the same chrome plating bath. Therefore, chrome plated parts having excellent corrosion resistance and heat resistance can be produced efficiently.

In the above-mentioned embodiment, hard chrome plating is conducted in two steps so as to form the two chrome layers  $S_1$  and  $S_2$ . However, in the present invention, the upper chrome layer  $S_2$  may be omitted and only the chrome layer  $S_1$  may be formed on the work W. In this case, the

crack-free chrome layer  $S_1$  is exposed to the outside and there is no oil sump for holding lubricating oil as in the case of the upper chrome layer  $S_2$  being formed on the lower chrome layer  $S_1$ . However, the chrome layer  $S_1$  is

5 satisfactory in terms of corrosion resistance.

Further, in the first embodiment, the lower chrome layer  $S_1$  and the upper chrome layer  $S_2$  are formed by continuous operation using the apparatus shown in Fig. 3. However, in the present invention, a single plating tank

10 containing a chrome plating bath may be prepared and the lower chrome layer  $S_1$  and the upper chrome layer  $S_2$  may be formed by batchwise operation using this plating tank. In this case, an output of a current source is controlled by means of a controller so that a desired current density

15 pattern of an applied current, such as that shown in Fig. 2, can be obtained.

For batchwise operation, instead of using a single plating tank, a plating tank for forming the lower chrome layer  $S_1$  and a plating tank for forming the upper chrome

20 layer  $S_2$  may be separately provided, and the lower chrome layer  $S_1$  and the upper chrome layer  $S_2$  may be formed by applying a pulse current to the plating tank for forming the lower chrome layer  $S_1$  and applying a direct current to the plating tank for forming the upper chrome layer  $S_2$ .

25 Fig. 4 shows a chrome plated part according to a second embodiment of the present invention. A feature of this embodiment resides in that two intermediate chrome layers  $S_3$  and  $S_4$  are provided between the lower chrome layer



$S_1$  and the upper chrome layer  $S_2$ . The properties of the intermediate chrome layers  $S_3$  and  $S_4$  are not particularly limited. However, it is preferred that the intermediate chrome layer  $S_3$  on a side of the lower chrome layer  $S_1$  has properties similar to those of the lower chrome layer  $S_1$  and the intermediate chrome layer  $S_4$  on a side of the upper chrome layer  $S_2$  has properties similar to those of the upper chrome layer  $S_2$ . Therefore, a few cracks  $F$  may be present in the intermediate chrome layer  $S_4$ .

By providing the intermediate chrome layers  $S_3$  and  $S_4$  between the lower chrome layer  $S_1$  and the upper chrome layer  $S_2$ , direct propagation of cracks from the upper chrome layer  $S_2$  to the lower chrome layer  $S_1$  can be suppressed, so that corrosion resistance of the chrome plated part can be stably maintained. Although the two intermediate layers  $S_3$  and  $S_4$  are provided in this embodiment, the number of intermediate chrome layers is not specifically limited in the present invention. A single intermediate layer or three or more intermediate layers may be provided.

A chrome plated part in the second embodiment of the present invention can be obtained by, for example, setting zones  $C_1$  and  $C_2$  between the above-mentioned zones A and B (Fig. 2) as shown in Fig. 5 and setting a waveform of a pulse current in the zones  $C_1$  and  $C_2$  to the pattern different from that in the zone A. With respect to an apparatus for obtaining the chrome plated part in the second embodiment, substantially the same apparatus as the apparatus of Fig. 3 can be used, except that the front bus

bar 9A (Fig. 3) corresponding to the plating process tank 4B is divided into a plurality of bus bars which are connected to different pulse current sources 12.

Fig. 6 is a chrome plated part according to a third embodiment of the present invention. A feature of this embodiment resides in that an oxide film  $S_3$  containing  $Cr_2O_3$  as a main component is formed as an outermost layer of the chrome plated part. The oxide film  $S_3$  is formed by conducting a heat oxidation process after polishing (buffing) of the upper chrome layer  $S_2$ . Due to the presence of the oxide film  $S_3$  as the outermost layer of the chrome plated part, corrosion resistance of the upper chrome layer  $S_2$  itself can be improved, to thereby prevent formation of white rust which is caused by corrosion of the chrome layer.

In the present invention, the oxide film may be formed solely from  $Cr_2O_3$ . Needless to say, when the oxide film contains not only  $Cr_2O_3$ , but also a component other than  $Cr_2O_3$  in a small amount, the oxide film is still satisfactory in terms of strength.

In order to conduct polishing and heat oxidation, an apparatus such as shown in Fig. 7 can be employed. This apparatus comprises a primary line  $L_1$  of production; a centerless polishing disk apparatus 20 provided in the primary line  $L_1$ ; a secondary line  $L_2$  of production provided in parallel to the primary line  $L_1$ ; a pusher 21, a high-frequency coil 22 and a cooling coil 23 provided in the secondary line  $L_2$ ; and an inclined stand-by member 24 connected to the primary line  $L_1$  and the secondary line  $L_2$ .

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The centerless polishing disk apparatus 20 comprises a buff wheel 20a and a regulating wheel 20b. After completion of the chrome plating process, the work W is polished between the buff wheel 20a and the regulating wheel 20b of the centerless polishing disk apparatus 20 and rolls on the inclined stand-by member 24 to the secondary line  $L_2$ , where the work W is continuously moved through the high-frequency coil 22 and the cooling coil 23 by extension of a rod 21a of the pusher 21. Thus, polishing and heat oxidation can be efficiently conducted.

#### Example 1

Using rods (diameter: 12.5 mm; length: 200 mm) made of steel (JIS S25C) as test pieces and a chrome plating bath comprising 250 g/L of chromic acid, 2.5 g/L of sulfuric acid, 8 g/L of organic sulfonic acid and 10 g/L of boric acid, pulse plating was conducted under the following conditions: bath temperature = 60°C; maximum current density  $I_u = 120$  A/dm<sup>2</sup>; minimum current density  $I_L = 0$  A/dm<sup>2</sup> (the same as in the case of Fig. 2); pulse time (on-time)  $T_1$  at maximum current density  $I_u = 100$  to 800  $\mu$ s; pulse time (off-time)  $T_2$  at minimum current density  $I_L = 100$  to 500  $\mu$ s; and frequency = 0.8 to 5.0 kHz. As a result, a lower chrome layer  $S_1$  (Fig. 1) having a thickness of about 3  $\mu$ m was formed on a surface of each test piece. Subsequently, in the same chrome plating bath, general-purpose plating was conducted at a bath temperature of 60°C and a current density of 60 A/dm<sup>2</sup>. As a result, an upper chrome layer  $S_2$  (Fig. 1) having a thickness of about 10  $\mu$ m was formed on the lower chrome

layer  $S_1$  on each test piece, to thereby obtain samples 2 to 18 (as shown in Table 2). Further, for reference, using the same test piece and chrome plating bath as mentioned above, general-purpose hard chrome plating was conducted at a bath temperature of  $60^{\circ}\text{C}$  and a current density of  $60 \text{ A/dm}^2$ . As a result, a single chrome layer having a thickness of about  $20 \mu\text{m}$  was formed on a surface of the test piece, to thereby obtain a sample 1.

With respect to the samples 2 to 18, a surface hardness (HV) was measured and visual observation was made by using a microscope to evaluate formation of cracks in each of the lower and upper chrome layers  $S_1$  and  $S_2$ . Further, with respect to the lower chrome layer  $S_1$ , residual stress and crystal grain size were measured as mentioned below. Further, the samples 2 to 18 were subjected to a salt-spray test in accordance with JIS Z2371, and visually observed to evaluate occurrence of rusting. With respect to the samples in which no rusting was observed, they were subjected to heat treatment at  $200^{\circ}\text{C}$  for 2 hours. The resultant samples were visually observed to evaluate formation of cracks on each of the lower and upper chrome layers  $S_1$  and  $S_2$  in the above-mentioned manner, and were subjected to the salt-spray test in accordance with JIS Z2371 again to evaluate occurrence of rusting. The color of a surface of each of the samples 2 to 18 was observed at the time of completion of formation of the lower chrome layer  $S_1$ . The above-mentioned measurements and observations were also conducted with respect to the single chrome layer of the sample 1.

Measurement of residual stress in the chrome layer was conducted by a method called "X-Sen Ouryoku Sokuteihou (X-ray stress measurement method)" disclosed in "Hihakai Kensa (non-destructive inspection)", vol. 37, item 8, pages 636 to 642, edited by The Japanese Society for Non-destructive Inspection. Measurement of a crystal grain size of the chrome layer was conducted using an X-ray diffractometer, by using a characteristic X-ray Cu-K $\alpha$  (wavelength: 1.5405620 Å) with respect to the Cr (222) diffraction plane. In this measurement, the crystal grain size was determined by assigning the result of measurement of the width (integral width) of a diffraction profile to the following Scherrer's equation. As the integral width, a value corrected by a Cauchy function was used.

$$D_{hkl} = K \cdot \lambda / \beta_1 \cos \theta$$

wherein  $D_{hkl}$ : crystal grain size (Å) [measured in a direction perpendicular to (hkl)]

$\lambda$ : wavelength of an X-ray for measurement (Å)

$\beta_1$ : width (integral width) of a diffraction beam dependent on the crystal grain size (rad)

$\theta$ : Bragg angle of the diffraction beam

K: constant (1.05)

Results of the above-mentioned measurements and observations are shown in Table 2.

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Sample No.	Pulse time ( $\mu$ s)		Crystal grain size of $S_1$ (nm)	Cracking of $S_1$	Residual stress (MPa)	Hard- ness (HV)	Appear- ance of $S_1$	Rusting		Evalu- ation
	$T_1$	$T_2$						Before heat treatment	After heat treatment	
1 (Comparative)			6.1	Observed	+230	1,090	Glossy	Observed (2h)		NG
2 (Comparative)	100	100	7.8	Observed	+276	1,034	Glossy	Observed (24h)		NG
3 (Comparative)	200	100	8.0	Observed	+160	1,017	Glossy	Observed (24h)		NG
4 (Comparative)	150	150	8.2	Observed	+10	940	Glossy	Observed (96h)		NG
5 (Comparative)	200	200	8.7	Not observed	-65	920	Glossy	Not observed (300h)	Observed (24h)	NG
6 (Present invention)	150	200	9.6	Not observed	-150	870	Glossy	Not observed (300h)	Not observed (300h)	OK
7 (Present invention)	100	200	9.8	Not observed	-203	835	Glossy	Not observed (300h)	Not observed (300h)	OK
8 (Present invention)	110	220	10.1	Not observed	-220	840	Glossy	Not observed (300h)	Not observed (300h)	OK
9 (Present invention)	800	300	10.5	Not observed	-205	818	Glossy	Not observed (300h)	Not observed (300h)	OK

Table 2 (1)

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Sample No.	Pulse time (μs)		Crystal grain size of S <sub>1</sub> (nm)	Cracking of S <sub>1</sub>	Residual stress (MPa)	Hardness (HV)	Appearance of S <sub>1</sub>	Rusting		Evaluation
	T <sub>1</sub>	T <sub>2</sub>						Before heat treatment	After heat treatment	
10 (Present invention)	400	300	10.6	Not observed	-305	782	Glossy	Not observed (300h)	Not observed (300h)	OK
11 (Present invention)	200	300	11.1	Not observed	-339	742	Glossy	Not observed (300h)	Not observed (300h)	OK
12 (Present invention)	300	300	11.7	Not observed	-313	710	Glossy	Not observed (300h)	Not observed (300h)	OK
13 (Present invention)	600	400	12.3	Not observed	-323	681	Glossy	Not observed (300h)	Not observed (300h)	OK
14 (Present invention)	500	400	13.5	Not observed	-334	630	Glossy	Not observed (300h)	Not observed (300h)	OK
15 (Present invention)	400	400	15.4	Not observed	-272	602	Glossy	Not observed (300h)	Not observed (300h)	OK
16 (Comparative)	300	400	16.0	Observed	+30	546	Milky	Observed (96h)		NG
17 (Comparative)	600	500	16.7	Observed	+53	498	Milky	Observed (96h)		NG
18 (Comparative)	700	500	18.1	Observed	+18	450	Milky	Observed (96h)		NG

Table 2 (2)

As shown in Table 2, with respect to the sample 1 (comparative) obtained by general-purpose hard chrome plating, the chrome layer contained many cracks and rusting was observed over an entire surface of the chrome layer at an extremely early time (2 hours) in the salt-spray test.

The samples 2 to 18 were obtained by the two-step plating process. Of these, with respect to the samples 2 to 4 and 16 to 18 (comparative), at the time of completion of the plating process, the upper chrome layer  $S_2$  contained many cracks and the lower chrome layer  $S_1$  was also cracked. When the samples 2 to 4 and 16 to 18 were subjected to the salt-spray test after the plating process, rusting was observed at a relatively early time (24 to 96 hours) in the salt-spray test. Thus, with respect to the samples 2 to 4 and 16 to 18, rusting occurred in the salt-spray test before heat treatment. Therefore, no heat treatment was conducted with respect to these samples.

On the other hand, with respect to the samples 5 to 15 also obtained by the two-step plating process, at the time of completion of the plating process, the upper chrome layer  $S_2$  contained many cracks, but no cracking was observed in the lower chrome layer  $S_1$ . Further, with respect to the samples 5 to 15, no rusting was observed until 300 hours after the start of the salt-spray test.

With respect to the samples 5 to 15 in which no rusting was observed before heat treatment, they were subjected to heat treatment at 200°C for 2 hours and visually observed to evaluate formation of cracks and



occurrence of rusting. With respect to the sample 5 (comparative), cracking was observed in the lower chrome layer  $S_1$  and rusting occurred at a relatively early time (24 hours) in the salt-spray test. On the other hand, with respect to the samples 6 to 15 (present invention), no cracking was observed in the lower chrome layer  $S_1$  even after heat treatment and no rusting was observed until 300 hours after the start of the salt-spray test.

Comparison was made between the samples 1 to 18 with respect to residual stress in the lower chrome layer  $S_1$  (the single chrome layer in the case of the sample 1). With respect to the samples 1 to 4 and 16 to 18 (comparative), the residual stress was tensile residual stress. With respect to the samples 5 to 15, the residual stress was compressive residual stress. Especially, the samples 6 to 15 (present invention) had a large compressive residual stress of 150 MPa or more.

Further, comparison was made between the samples 1 to 18 with respect to a crystal grain size of the lower chrome layer  $S_1$  (the single chrome layer in the case of the sample 1). With respect to the samples 1 to 5 (comparative), the crystal grain size was less than 9 nm. With respect to the samples 6 to 18, the crystal grain size was 9 nm or more. In each of the samples 16 to 18, the chrome layer had an especially large crystal grain size of 16 nm or more.

With respect to the surface hardness (HV), the surface hardness of the sample 1 (obtained by general-purpose hard plating) was the highest. With respect to the remaining

samples, the larger the crystal grain size, the lower the surface hardness.

Further, comparison was made between the samples 1 to 18 with respect to the color of a surface of the lower chrome layer  $S_1$  (the single chrome layer in the case of the sample 1). With respect to the samples 1 to 15, the chrome layer had a glossy surface characteristic of chrome plating. With respect to the samples 16 to 18, the chrome layer had a milky surface.

From the above, it is apparent that formation of cracks in the chrome layer is dependent on the residual stress and the crystal grain size of the chrome layer. In order to ensure a desired corrosion resistance of the chrome plated part by suppressing cracking of the chrome layer even when it is subject to thermal hysteresis, it is necessary to conduct the chrome plating process so that the lower chrome layer  $S_1$  having a compressive residual stress of 150 MPa or more, and preferably having a crystal grain size of 9 nm or more can be obtained. The compressive residual stress which can be obtained solely by adjusting the waveform of a pulse current is limited. Therefore, an appropriate waveform of a pulse current must be selected, depending on the intended applications of the chrome plated part. With respect to the crystal grain size, the lower chrome layer of each of the samples 16 to 18, which had a crystal grain size of 16 nm or more, had tensile residual stress. Therefore, it is preferred that the crystal grain size be less than 16 nm.

Example 2

Using the same test piece and chrome plating bath as used in Example 1, pulse plating was conducted under the following conditions: bath temperature = 60°C; maximum current density  $I_v = 120 \text{ A/dm}^2$ ; minimum current density  $I_L = 0 \text{ A/dm}^2$ ; pulse time (on-time)  $T_1$  at maximum current density  $I_v = 1,400 \text{ } \mu\text{s}$ ; pulse time (off-time)  $T_2$  at minimum current density  $I_L = 600 \text{ } \mu\text{s}$ ; and frequency = 500 Hz. As a result, a lower chrome layer  $S_1$  (Fig. 4) having a thickness of about 2  $\mu\text{m}$  was formed on a surface of the test piece. Subsequently, in the same chrome plating bath, pulse plating was conducted under the following conditions: bath temperature = 60°C; maximum current density  $I_v = 120 \text{ A/dm}^2$ ; minimum current density  $I_L = 0 \text{ A/dm}^2$ ; on-time  $T_1 = 1,400 \text{ } \mu\text{s}$ ; off-time  $T_2 = 400 \text{ } \mu\text{s}$ ; and frequency = 625 Hz. As a result, an intermediate chrome layer  $S_3$  (Fig. 4) having a thickness of about 2  $\mu\text{m}$  was formed on a surface of the lower chrome layer  $S_1$ . Subsequently, in the same chrome plating bath, pulse plating was conducted under the following conditions: bath temperature = 60°C; maximum current density  $I_v = 120 \text{ A/dm}^2$ ; minimum current density  $I_L = 0 \text{ A/dm}^2$ ; on-time  $T_1 = 200 \text{ } \mu\text{s}$ ; off-time  $T_2 = 100 \text{ } \mu\text{s}$ ; and frequency = 3,333 Hz. As a result, an intermediate chrome layer  $S_4$  (Fig. 4) having a thickness of about 2  $\mu\text{m}$  was formed on a surface of the intermediate chrome layer  $S_3$ . Subsequently, in the same chrome plating bath, general-purpose plating was conducted at a bath temperature of 60°C and a current density of 60  $\text{A/dm}^2$ . As a result, an upper chrome layer  $S_2$  (Fig. 4) having a thickness

of about 5  $\mu\text{m}$  was formed on the intermediate chrome layer  $S_4$ , to thereby obtain a sample.

With respect to the obtained sample, each of the lower chrome layer  $S_1$ , the intermediate chrome layers  $S_3$  and  $S_4$  and the upper chrome layer  $S_2$  was visually observed by using a microscope to evaluate formation of cracks. Further, by the same methods as mentioned above in Example 1, residual stress and crystal grain size were measured with respect to each of the chrome layers  $S_1$  to  $S_4$ . The sample was subjected to the salt-spray test in accordance with JIS Z2371, and visually observed to evaluate occurrence of rusting. After the salt-spray test, the sample was subjected to heat treatment at 200°C for 2 hours, and subjected to the salt-spray test in accordance with JIS Z2371 again. The resultant sample was visually observed to evaluate occurrence of rusting. Results of the above-mentioned measurements and observations are shown in Table 3.

Table 3

Chrome layer	Residual stress (MPa)	Crystal grain size (nm)	Cracking	Rusting	
				Before heat treatment	After heat treatment
$S_1$	-279	12.2	Not observed	Not observed	Not observed
$S_3$	-163	10.7	Not observed		
$S_4$	+226	8.0	Slightly observed		
$S_2$	+300	6.6	Observed		

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As shown in Table 3, no cracking was observed with respect to the lower chrome layer  $S_1$  and the intermediate chrome layer  $S_3$ . The intermediate chrome layer  $S_4$  on a side of the upper chrome layer  $S_2$  was slightly cracked and the upper chrome layer  $S_2$  contained many cracks. With respect to the residual stress, each of the lower chrome layer  $S_1$  and the intermediate chrome layer  $S_3$  had compressive residual stress as large as more than 150 MPa. Each of the intermediate chrome layer  $S_4$  and the upper chrome layer  $S_2$  had tensile residual stress. With respect to the crystal grain size, the crystal grain size of each of the lower chrome layer  $S_1$  and the intermediate chrome layer  $S_3$  was as large as more than 9 nm. The crystal grain size of each of the intermediate chrome layer  $S_4$  and the upper chrome layer  $S_2$  was much smaller than 9 nm.

No rusting was observed in the salt-spray test before and after heat treatment. Therefore, it was understood that the sample had sufficient corrosion resistance.

### Example 3

Using the same test pieces and chrome plating bath as used in Example 1, pulse plating was conducted under the following conditions: bath temperature = 60°C; maximum current density  $I_v = 120 \text{ A/dm}^2$ ; minimum current density  $I_L = 0 \text{ A/dm}^2$ ; pulse time (on-time)  $T_1$  at maximum current density  $I_v = 300 \text{ } \mu\text{s}$ ; pulse time (off-time)  $T_2$  at minimum current density  $I_L = 300 \text{ } \mu\text{s}$ ; and frequency: 1.7 kHz. As a result, a crack-free lower chrome layer  $S_1$  (Fig. 1) having a thickness of about 3  $\mu\text{m}$  was formed on a surface of each test piece.

Subsequently, in the same chrome plating bath, general-purpose plating was conducted at a bath temperature of 60°C and a current density of 60 A/dm<sup>2</sup>. As a result, a cracked upper chrome layer S<sub>2</sub> (Fig. 1) having a thickness of about 10 μm was formed on the lower chrome layer S<sub>1</sub> on each test piece. The upper chrome layer S<sub>2</sub> was finished by buffing so as to have a surface roughness Ra of 0.08 μm. As a result, samples 31 and 32 were obtained. The sample 31 was subjected to a general-purpose baking process at 210°C for 4 hours, to thereby form an oxide film (containing Cr<sub>2</sub>O<sub>3</sub> as a main component) on the upper chrome layer S<sub>2</sub>. The sample 32 was subjected to high-frequency heating at a maximum heating temperature of 400°C for a short period of time (about 10 seconds), to thereby form an oxide film (containing Cr<sub>2</sub>O<sub>3</sub> as a main component) on the upper chrome layer S<sub>2</sub>.

For comparison, using the same test piece and chrome plating bath as used in Example 1, pulse plating was conducted under the following conditions: bath temperature = 60°C; maximum current density I<sub>u</sub> = 120 A/dm<sup>2</sup>; minimum current density I<sub>L</sub> = 0 A/dm<sup>2</sup>; on-time T<sub>1</sub> = 200 μs; off-time T<sub>2</sub> = 200 μs; and frequency = 2.5 kHz. As a result, a cracked lower chrome layer S<sub>1</sub> having a thickness of about 3 μm was formed on a surface of the test piece. Subsequently, in the same chrome plating bath, general-purpose plating was conducted at a bath temperature of 60°C and a current density of 60 A/dm<sup>2</sup>. As a result, a cracked upper chrome layer S<sub>2</sub> having a thickness of about 10 μm was formed on a surface of the lower chrome layer S<sub>1</sub>, to thereby obtain a sample 33. The

sample 33 was subjected to the above-mentioned buffing and high-frequency heating. Further, for comparison, substantially the same procedure for obtaining the sample 31 was repeated, except that the baking process was conducted  
5 before buffing, to thereby obtain a sample 34.

With respect to each of the samples 31 to 34, residual stress and crystal grain size of the lower chrome layer  $S_1$  were measured by the same methods as mentioned above in Example 1. The samples 31 to 34 were subjected to the salt-spray test in accordance with JIS Z2371, and visually  
10 observed to evaluate formation of red rust and white rust. Results of the above-mentioned measurements and observations are shown in Table 4.

Table 4

Sample No.	Process	Crystal grain size of $S_1$ (nm)	Residual stress of $S_1$ (MPa)	Method of heat oxidation	Rusting	
					White rust	Red rust
31	Plating-Polishing-Oxidation	11.7	-313	Baking	Not observed	Not observed
32	Plating-Polishing-Oxidation	11.7	-313	High-frequency heating	Not observed	Not observed
33	Plating-Polishing-Oxidation	8.7	-65	High-frequency heating	Not observed	Observed
34	Plating-Oxidation-Polishing	8.7	-65	Baking	Observed	Not observed

As shown in Table 4, in each of the samples 31 and 32, the lower chrome layer  $S_1$  had sufficiently large compressive residual stress and a sufficiently large crystal grain size. On the other hand, in each of the samples 33 and 34, the lower chrome layer  $S_1$  had undesirably low compressive residual stress and an undesirably small crystal grain size.

After the salt-spray test, with respect to each of the samples 31 and 32 (present invention), red rust which forms due to corrosion of a metallic substrate and white rust which forms due to corrosion of the chrome layer were not observed. On the other hand, red rust was observed in the sample 33 (comparative) and white rust was observed in the sample 34 (comparative). Red rust was observed in the sample 33 because both of the lower chrome layer  $S_1$  and the upper chrome layer  $S_2$  contained cracks. White rust was observed in the sample 34 because the oxide film formed by the baking process was removed by buffing. Fig. 8 is a microphotograph showing white rust formed in the sample 34. No red rust was observed in the sample 34 because, during buffing, the cracks were clogged due to the occurrence of plastic flow in the chrome layer.

Fig. 9 is a graph showing a relationship between the thickness of plating and residual stress in the chrome plated part of the present invention when pulse plating is conducted by application of the same pulse current as used for obtaining the sample 12. In the graph, there is substantially no stress gradient such as that shown in the above-mentioned Examined Japanese Patent Application



Publication No. 43-20082. Average compressive residual stress is stably maintained at a level of 100 MPa or more.

As has been described above, the chrome plated part of the present invention maintains excellent corrosion

5 resistance even when it is subject to thermal hysteresis.

Therefore, the present invention is advantageous when applied to products used in corrosive environments and under high temperature conditions. The chrome plated part of the present invention is especially advantageous when it

10 comprises a crack-free chrome layer provided as the lowermost chrome layer and a cracked chrome layer provided as the uppermost chrome layer, because such a chrome plated part has excellent wear resistance and excellent sliding properties.

15 In the chrome plating method of the present invention, compressive residual stress and crystal grain size of the chrome layer can be easily controlled by adjusting the waveform of a pulse current. Therefore, a chrome plated part having desired properties can be efficiently obtained.

20 Further, in the method of the present invention for producing a chrome plated part, an oxide film containing  $\text{Cr}_2\text{O}_3$  may be formed as an outermost layer of the chrome plated part. Therefore, formation of red rust due to corrosion of a metallic substrate and formation of white  
25 rust due to corrosion of the chrome layer can be surely prevented.

The present invention can be applied to a surface of a piston rod for a shock absorber or a surface of a piston ring

for an engine.

The entire disclosures of Japanese Patent Application  
Nos. 10-332047 and 11-285503 filed on November 6, 1998 and  
October 6, 1999, respectively, each including a  
5 specification, claims, drawings and summary are incorporated  
herein by reference in their entirety.

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